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Plane Grating Monochromator of Littrow Type

Keiei KUDO

Institute for Optical Research. Tokyo Universtity of Education
Shinzyuku-ku, Tokyo

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Abstract

The aberration of plane grating monochromator of Littrow type is approximately calculated, and expressions for dispersion, image form and focal plane are obtained. By the use of these expressions the arrangement and length of entrance and exit slits are discussed.

1. Introduction

In the previous work[1] the aberration of plane grating monochromators such as of Ebert, Pfund and Czerny-Turner type was calculated in the case of symmetric arrangement. Littrow arrangement was examined and compared with that of the above monochromators. There are a few reports[2)~4)] on the image formation and ray tracing[5] in Littrow system, which however do not enlighten us on the subjects how the image is affected when arrangement of slits is changed and how the astigmatism can be made small when an off-axis paraboloidal mirror is used. In this paper, these matters concerning practical working arrangements are treated.

2. General Expression

As shown in Fig. 1, the origin of a rectangular system is taken at the apex of paraboloidal mirror and x-axis is taken to coincide with the mirror axis. Then the paraboloidal mirror surface with focal length f is

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1) K. Kudo: Science of Light **9**, 1 (1960).
2) H. M. Randall and F. A. Firestone: Rev. Sci. Inst. **9**, 404 (1938).
3) R. Minskowski: Astrophys. J. **96**, 306 (1952).
4) C. S. Rupert: J. Opt. Soc. Am. **42**, 779 (1952).
5) H. Yoshinaga, B. Okazaki and S. Tatsuoka: J. Opt. Soc. Am. **50**, 437 (1960).
(According to a letter from Prof. H. Yoshinaga to the editor, these are typographical errors in the print: Equation (5) should read $\xi'=\xi-2l(\xi l+\eta m+\zeta n), \ldots$).

$$4fx = y^2 + z^2 \tag{1}$$

Therefore the direction consines of the normal to the mirror surface at the point (xyz) are

$$L = -2f/R, \quad M = y/R, \quad N = z/R \tag{2}$$

where

$$R^2 \equiv 4f(f+x) \tag{3}$$

If the coordinates of object (entrance slit) S_1 and grating G are $(x_1y_1z_1)$ and $(\xi\eta l)$

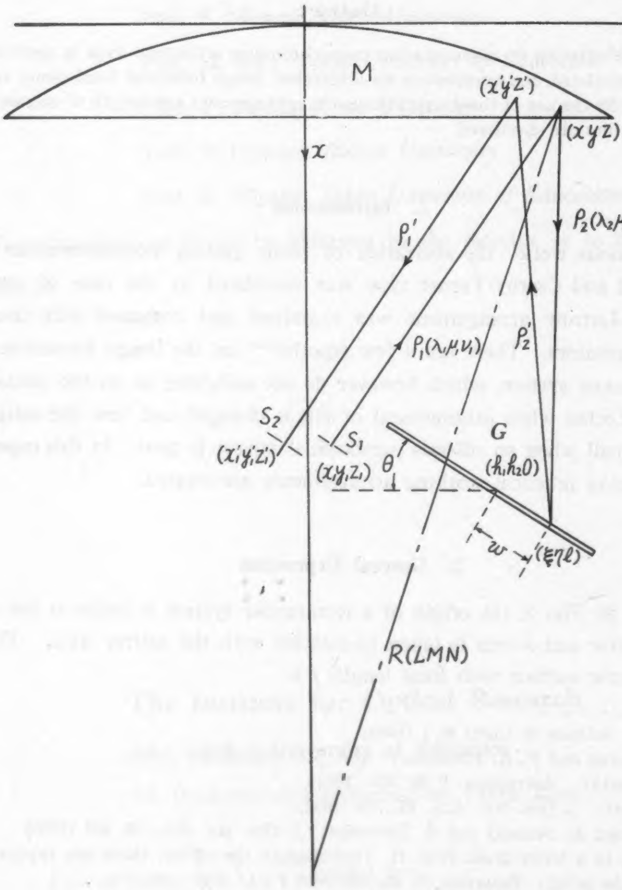

Fig. 1. Coordinates of optical elements in Littrow system.

respectively, incident light path ρ_1 and reflected light path ρ_2 become

$$\rho_1^2 = x_1^2 + y_1^2 + z_1^2 + x^2 + 2F_0x - 2(y_1y + z_1z) \tag{4}$$

$$\rho_2^2 = \xi^2 + \eta^2 + l^2 + x^2 + 2(2f - \xi)x - 2(y_1\eta + lz) \tag{5}$$

where

$$F_0 \equiv 2f - x_1 \tag{6}$$

Therefore the direction cosines of the incident and reflected lights are

$$\lambda_1 = (x - x_1)/\rho_1, \qquad \mu_1 = (y - y_1)/\rho_1, \qquad \nu_1 = (z - z_1)/\rho_1 \tag{7}$$

$$\lambda_2 = (\xi - x)/\rho_2, \qquad \mu_2 = (\eta - y)/\rho_2, \qquad \nu_2 = (l - z)/\rho_2 \tag{8}$$

If the coordinates of the grating center are $(h_1\, h_2\, 0)$,

$$\begin{aligned} \xi &= h_1 + w\phi_1 \qquad & \phi_1 &\equiv \sin\theta \\ \eta &= h_2 + w\phi_2 \qquad & \phi_2 &\equiv \cos\theta \end{aligned} \tag{9}$$

Reflection law is

$$(\mu_2 - \mu_1)/2L = (\lambda_2 - \lambda_1)/2M \tag{10}$$

$$= (\nu_2 - \nu_1)/2N \tag{11}$$

$$= -(L\lambda_1 + M\mu_1 + N\nu_1) \tag{12}$$

Therefore from (10) (1) (2) (7) and (8)

$$y = \frac{1}{a}\left\{\eta + \left(\frac{2fa - (x_1 - \xi)}{F_0} X^{-1} - 1\right) y_1\right\} \tag{13}$$

Similarly, from (11) (1) (2) (7) (8) and (13)

$$z = \frac{1}{a}\left\{l + \left(\frac{2fa(x_1 - \xi)}{F_0} X^{-1} - 1\right) z_1\right\} \tag{14}$$

where

$$a \equiv \{x + 2f - \xi + (\rho_2/\rho_1)(x + 2f - x_1)\}/2f \tag{15}$$

$$X \equiv 1 + x/2F_0 \tag{16}$$

Therefore, from (1)

$$X^3 - X^2\left(1 + \frac{G - 2K + S}{4fF_0a^2}\right) - X\frac{2fa - (x_1 - \xi)}{2fF_0^2a^2}(K - S) - \frac{\{2fa - (x_1 - \xi)\}^2}{4fF_0^3a^2}S = 0 \tag{17}$$

where,

$$G \equiv \eta^2 + l^2, \qquad K \equiv \eta y_1 + lz_1, \qquad S \equiv y_1^2 + z_1^2 \tag{18}$$

From (12) (1) (2), (7) (8) (13) and (14)

$$a^2\left\{X^3-\frac{f-x_1}{F_0}X^2-\frac{2f(f-x_1)}{F_0^2}X-\frac{2f}{F_0^3}S\right\}-a\left\{X^3-\frac{2(f-x_1)}{F_0}X^2\right.$$
$$\left.-\frac{(f-x_1)(x_1-\xi)-(K-2S)}{F_0^2}X-\frac{2(x_1-\xi)}{F_0^3}S\right\}$$
$$+\frac{1}{2fF_0}\left\{(K-S)X^2+\frac{(x_1-\xi)}{F_0}(K-2S)X-\frac{(x_1-\xi)^2}{F_0^2}S\right\}=0 \tag{19}$$

Since the predominant part of x is $(1/4f)\ (G+2K\xi/F_0+S\xi^2/F_0^2)$, from (17) and (19) approximate solutions of x and a, therefore y (13) and z (14), are obtained. Hence from (4) and (5)

$$\rho_1+\rho_2=\rho_{10}+\rho_{20}+(\psi_{10}\phi_1+\psi_{11}\phi_2)w+\psi_{12}z_1l+(\psi_{20}\phi_1^2+\psi_{21}\phi_2^2+\psi_{22}\phi_1\phi_2)w^2$$
$$+(\psi_{23}\phi_1+\psi_{24}\phi_2)wz_1l+\psi_{25}l^2+\cdots\cdots \tag{20}$$

where

$$\rho_{10}^2\equiv\rho_{100}^2+y_1\rho_{101}+y_1^2\rho_{102}+z_1^2\rho_{103}+y_1^3\rho_{104}+y_1z_1^2\rho_{105}+y_1^2z_1^2\rho_{106}+\cdots\cdots \tag{21}$$

$$\rho_{100}^2\equiv\sigma_0^2-4f(f-x_1)\,,\qquad \sigma_0\equiv F_0+\frac{h_2^2}{4f}\,,$$

$$\rho_{101}\equiv-2h_2+\sigma_0\left(\frac{h_2}{F_0}-\frac{h_2(f-h_1)}{fF_0}-\frac{3h_2^3}{2fF_0^2}+\frac{h_2^3(f-h_1)}{2f^2F_0^2}+\cdots\cdots\right)$$

$$\rho_{102}\equiv-1+\frac{2(f-h_1)}{F_0}+\frac{9h_2^2}{4F_0^2}-\frac{2h_2^2(f-h_1)}{fF_0^2}-\frac{5h_2^4}{4fF_0^3}+\frac{h_2^2(f-h_1)^2}{4f^2F_0^2}+\cdots\cdots$$
$$+\sigma_0\left(\frac{f}{2F_0^2}-\frac{f-h_1}{F_0^2}-\frac{7h_2^2}{4F_0^3}+\frac{x_1^2h_2^2}{4f^2F_0^3}+\frac{(f-h_1)^2}{2fF_0^2}+\frac{11h_2^2(f-h_1)}{2fF_0^3}+\cdots\cdots\right)$$

$$\rho_{103}\equiv1-2\left(\frac{f}{F_0}+\frac{f-h_1}{F_0}-\frac{h_2^2}{2fF_0}+\frac{h_2^2(f-h_1)}{4fF_0^2}+\frac{h_2^4}{8f^2F_0^2}+\cdots\cdots\right)$$
$$+\sigma_0\left(\frac{f}{4F_0^2}-\frac{f-h_1}{2F_0^2}-\frac{5h_2^2}{8F_0^3}+\frac{(f-h_1)^2}{4fF_0^2}+\frac{3h_2^2(f-h_1)}{4fF_0^3}-\frac{3h_2^2(f-h_1)^2}{8f^2F_0^3}+\cdots\cdots\right)$$

$$\vdots$$

$$\rho_{20}^2\equiv\rho_{200}^2+y_1\rho_{201}+y_1^2\rho_{202}+z_1^2\rho_{203}+\cdots\cdots \tag{22}$$

$$\rho_{200}\equiv h_1-\frac{h_2^2}{4f}$$

$$\rho_{201}\equiv\frac{2fh_2}{F_0}-2h_2-\frac{h_2^3}{F_0^2}-\frac{h_2^3(f-h_1)}{2fF_0^2}-\frac{h_2^2(f-x_1)}{fF_0^2}-\frac{h_2^5}{2fF_0^3}+\cdots\cdots)$$

$$-\rho_{200}\left(\frac{h_2}{F_0}-\frac{h_2(f-h_1)}{fF_0}-\frac{2h_2^3}{fF_0^2}-\frac{h_2^3(f-x_1)}{2f^2F_0^2}+\frac{h_2^3(f-h_1)}{f^2F_0^2}+\cdots\cdots\right)$$

$$\rho_{202}\equiv\frac{f^2}{F_0^2}-\frac{2f(f-h_1)}{F_0^2}+\frac{(f-h_1)^2}{F_0^2}+\frac{x_1^2h_2^2}{2fF_0^3}-\frac{3fh_2^2}{2F_0^3}+\frac{h_2^2}{4F_0^2}+\frac{h_2^2(f-h_1)}{2fF_0^2}$$

$$-\frac{3h_2^4}{4fF_0^3}+\frac{h_2^2(f-h_1)^2}{4f^2F_0^2}+\frac{5h_2^2(f-h_1)}{F_0^3}+\frac{2h_2^2(f-h_1)(f-x_1)}{fF_0^3}$$

$$-\frac{33h_2^4}{4F_0^4}+\frac{3h_2^2(f-h_1)^2}{fF_0^3}+\cdots\cdots$$

$$-\rho_{200}\left(\frac{f}{2F_0^2}-\frac{f-h_1}{F_0^2}-\frac{7h_2^2}{4F_0^3}+\frac{x_1^2h_2^2}{4f^2F_0^3}+\frac{(f-h_1)^2}{2fF_0^2}+\frac{11h_2^2(f-h_1)}{2fF_0^3}+\cdots\right)$$

$$\rho_{203}\equiv\frac{f^2}{F_0^2}-\frac{2f(f-h_1)}{F_0^2}-\frac{3fh_2^2}{2F_0^3}+\frac{(f-h_1)^2}{F_0^2}+\frac{h_2^2(f-h_1)}{F_0^3}$$

$$-\frac{h_2^2(f-h_1)^2}{2fF_0^3}+\frac{2h_2^4}{F_0^4}+\cdots\cdots$$

$$-\rho_{200}\left(\frac{f}{4F_0^2}-\frac{f-h_1}{2F_0^2}-\frac{5h_2^2}{8F_0^3}+\frac{(f-h_1)^2}{4fF_0^2}+\frac{3h_2^2(f-h_1)}{4fF_0^3}+\cdots\cdots\right)$$

$$\phi_{10}\equiv1+y_1\left(-\frac{h_2^3}{4f^4}+\cdots\cdots\right)+y_1^2\left(-\frac{1}{2f^2}-\frac{f-h_1}{4f^3}+\frac{11h_2^2}{8f^4}\right)$$

$$+z_1^2\left(-\frac{1}{2f^2}+\frac{3h_2^2}{4f^4}+\cdots\cdots\right)+\cdots\cdots \tag{23}$$

$$\phi_{11}\equiv y_1\left(-\frac{1}{f}-\frac{2(f-x_1)}{f^2}+\frac{33h_2^2}{4f^3}+\frac{33h_2^2(f-h_1)}{4f^4}+\cdots\cdots\right)$$

$$+y_1^2\left(-\frac{17h_2}{2f^3}-\frac{3(f-h_1)}{2f^3}-\frac{4h_2^2+23h_2(f-h_1)}{8f^4}+\cdots\cdots\right)$$

$$+z_1^2\left(-\frac{11h_2(f-h_1)}{2f^4}+\cdots\cdots\right)+\cdots\cdots \tag{24}$$

$$\phi_{12}\equiv-\frac{1}{f}-\frac{2(f-h_1)}{f^2}-\frac{h_2^2}{4f^3}-\frac{2(f-x_1)}{f^2}-\frac{2(f-h_1)^2}{f^3}$$

$$-\frac{3h_2^2(f-h_1)}{4f^4}-\frac{2(f-h_1)^3}{f^4}+\cdots\cdots$$

$$+y_1\left(-\frac{2h_2}{f^3}-\frac{h_2(f-h_1)}{f^3}+\cdots\cdots\right)+\cdots\cdots \tag{25}$$

$$\phi_{21}\equiv\frac{1}{2f}\left\{\left(1-\frac{4f(f-x_1)}{\sigma_0^2}\right)^{-\frac{1}{2}}-1\right\}+\frac{h_2^2}{4f^2\sigma_0}\left\{\left(1-\frac{4f(f-x_1)}{\sigma_0^2}\right)^{-\frac{1}{2}}-\left(1-\frac{4f(f-x_1)}{\sigma_0^2}\right)^{-\frac{3}{2}}\right\}$$

$$+y_1\left(-\frac{h_2}{f^3}-\frac{h_2(f-x_1)}{f^4}+\cdots\cdots\right)+y_1^2\left(\frac{3}{2f^3}-\frac{15h_2}{16f^4}+\frac{71(f-h_1)}{8f^4}+\cdots\cdots\right)$$

$$+z_1^2\left(\frac{2}{f^3}+\frac{f-h_1}{2f^4}+\cdots\cdots\right)+\cdots\cdots \tag{26}$$

$$\psi_{25}\equiv y_1\left(-\frac{h_2}{4f^3}-\frac{h_2(f-h_1)}{f^4}+\cdots\cdots\right)+y_1^2\left(-\frac{1}{8f^3}+\frac{3(f-h_1)}{8f^4}+\cdots\cdots\right)$$

$$+z_1^2\left(-\frac{9}{8f^3}-\frac{39(f-h_1)}{8f^4}+\cdots\cdots\right)+\cdots\cdots \tag{27}$$

Similar expressions for ψ_{20}, ψ_{22}, ψ_{23}, and ψ_{24} can be obtained, but they are not given here because of no necessarity.

Since the diffracted light paths are expressed as $\rho_1'=\rho_1(y_1\to y_1',\ z_1\to z_1')$, $\rho_2'=\rho_2(y_1\to y_1',\ z_1\to z_1')$ and $\psi_{ij}'=\psi_{ij}(y_1\to y_1',\ z_1\to z_1')$, the optical path function L is

$$L=\rho_1+\rho_2+\rho_2'+\rho_1'+(n\lambda/d)w \tag{28}$$

Where n is the order number of spectrum, d the grating constant.

In ordinary monochromators, both $\partial L/\partial w=0$ and $\partial L/\partial l=0$ are not satisfied at the same time. Therefore, the optimum condition about the arrangement of optical parts is to be first determined by applying Fermat's principle to the low power terms of w and l in L, and next, the effect of other aberration is to be examined under such condition. For this purpose, L is conveniently devided into the following

$$L=F_1+F_2+F_3+\cdots\cdots \tag{29}$$

$$F_1\equiv\rho_{10}+\rho_{20}+\rho_{10}'+\rho_{20}'+\{(\psi_{10}+\psi_{10}')\phi_1+(\psi_{11}+\psi_{11}')\phi_2+(n\lambda/d)\}w$$
$$+(z_1\psi_{12}+z_1'\psi_{12}')l \tag{30}$$

$$F_2\equiv\{(\psi_{20}+\psi_{20}')\phi_1^2+(\psi_{21}+\psi_{21}')\phi_2^2+(\psi_{22}+\psi_{22}')\phi_1\phi_2\}w^2 \tag{31}$$

$$F_3\equiv(\psi_{25}+\psi_{25}')l^2 \tag{32}$$

3. Dispersion formula and image form

It will be shown later that $x_1=f+\Delta(y_1z_1)$ and $\Delta(y_1z_1)$ is very small. Therefore, dispersion formula and image form are not so much affected by $\Delta(y_1z_1)$. Thus dispersion formula and image form will be obtained as $x_1\approx f$. Applying Fermat's principle to (30), we obtain

$$-n\lambda/d=(\psi_{10}+\psi_{10}')\phi_1+(\psi_{11}+\psi_{11}')\phi_2 \tag{33}$$

$$0=z_1\psi_{12}+z_1'\psi_{12}' \tag{34}$$

Along the isochromat, it must be

$$-n\lambda/d=\{(\psi_{10}+\psi_{10}')\phi_1+(\psi_{11}+\psi_{11}')\phi_2\}_{z_1=z_1'=0} \tag{35}$$

Assuming that the object (entrance slit) is straight and parallel to z-axis (y_1=const.), and the image center is at $(x_{10}y_{10}0)$, we have from (35) (33) (23) and (24),

$$y_1'=y_{10}-\frac{z_1^2+z_1'^2}{2f}C_0\tan\theta \tag{36}$$

where

$$C_0\equiv\left(1-\frac{3h_2^2-22h_2(f-h_1)\cot\theta}{2f^2}\right)\left[1+\left\{y_{10}\left(\frac{1}{f}+\frac{f-h_1}{2f^2}-\frac{11h_2^2}{4f^3}\right)+\frac{h_2^3}{4f^3}\right\}\tan\theta\right.$$
$$\left.-\frac{33}{4}\left(\frac{h_2^2}{f^2}+\frac{h_2^2(f-h_1)}{f^3}\right)+y_{10}\left(\frac{17h_2+3(f-h_1)}{f^2}+\frac{4h_2^2+23h_2(f-h_1)}{4f^3}\right)\right]^{-1} \tag{37}$$

Remembering that if $z_1>0$, then $z_1'<0$, we have from (34)

$$z_1'^2=D_0z_1^2 \tag{38}$$

where

$$D_0\equiv1+\frac{4h_2(y_1-y_{10})}{f^2}\left(1-\frac{3(f-h_1)}{2f}+\cdots\cdots\right) \tag{39}$$

Therefore (36) becomes

$$y_1'-y_{10}=-\frac{z_1^2}{f}C_0D_0'\tan\theta \tag{40}$$

where

$$D_0'\equiv(1+D_0)/2$$

If y_1/f, h_2/f are negligibly small, $C_0=D_0'=1$. In such case, (40) is coincident with Randall's expression.

The radius of curvature r_0 at image center ($z_1'=0$) becomes

$$r_0=-\frac{f}{2}C_0^{-1}D_0'^{-1}\cot\theta \tag{41}$$

From (33), (38) and (40), the relation between grating angle θ and diffracted wavelength λ becomes

$$-n\lambda/d=2H_0\sin\theta \tag{42}$$

where

$$H_0\equiv1-(y_1+y_{10})\left[\left(\frac{1}{2f}-\frac{33h_2^2}{8f^3}-\frac{33h_2^2(f-h_1)}{8f^4}\right)\cot\theta+\frac{h_2^3}{8f^4}\right]$$
$$-(y_1^2+y_{10}^2)\left[\frac{1}{4f^2}+\frac{f-h_1}{8f^3}-\frac{11h_2^2}{16f^4}+\left(\frac{17h_2+3(f-h_1)}{4f^3}+\frac{4h_2^2+23h_2(f-h_1)}{16f^4}\right)\cot\theta\right]$$

$$-z_1^2\left[(1+D_0)\left(\frac{1}{4f^2}-\frac{3h_2^2}{8f^4}\right)-y_{10}C_0D_0'\left(\frac{1}{2f^3}+\frac{f-h_1}{4f^4}\right)\tan\theta\right.$$

$$\left.-C_0D_0'\left\{\frac{1}{2f^2}-\frac{33h_2^2}{8f^4}+y_{10}\frac{17h_2+3(f-h_1)}{2f^4}\right\}+\cdots\cdots\right]$$

Therefore, for minimizing the wavelength error caused by the way the slit is arranged, it must be $y_{10}=-y_1$.

4. Focal plane

From (31), the focal condition is

$$\{(\psi_{20}+\psi_{20}')\phi_1^2+(\psi_{21}+\psi_{21}')\phi_2^2+(\psi_{22}+\psi_{22}')\phi_1\phi_2\}\,w=0$$

The solution that always satisfies the above equation independently of w and θ should be

$$\psi_{20}+\psi_{20}'=\psi_{21}+\psi_{21}'=\psi_{22}+\psi_{22}'=0$$

In the first place, from $\psi_{21}+\psi_{21}'=0$ and from (38) (40) and (26), approximate value of x_1 becomes

$$\frac{x_1}{f}=1-\frac{1}{2f^2}\left(1+\frac{h_2^2}{4f^2}\right)^2\left[1-\frac{h_2^2}{f^2}\left(1+\frac{h_2^2}{4f^2}\right)^{-1}-\left(y_1+y_{10}-\frac{z_1^2}{f}C_0D_0'\tan\theta\right)\right.$$

$$\frac{h_2^2}{2f^2}\left(1+\frac{h_2^2}{4f^2}\right)^2\Bigg]^{-1}\left[h_2(y_1+y_{10})-(y_1^2+y_{10}^2)\left(\frac{3}{2}+\frac{142(f-h_1)-15h_2}{16f}\right)\right.$$

$$-z_1^2(1+D_0)\left(2+\frac{f-h_1}{2f}\right)-\frac{z_1^2}{f}C_0D_0'\tan\theta\,(h_2+3y_{10}+\cdots\cdots)$$

$$\left.-\frac{3z_1^4}{2f^2}C_0^2D_0'^2\tan^2\theta+\cdots\cdots\right],$$

$$\approx 1+\frac{3y_1^2+4z_1^2}{2f^2} \tag{43}$$

The focal condition (43) approximately satisfies both $\psi_{20}+\psi_{20}'=0$ and $\psi_{22}+\psi_{22}'=0$, From (43) we see that the focal point is slightly affected by y_1 and z_1.

5. Effect of Astigmatism

If the image form and the lie of the focal plane are once determined, arrangement of the optical components in the monochromator and the forms of entrance and exit slit are fixed, therefore, no means will be left to minimize the astigmatism. Under such circumstances, we have only to evaluate the amount of astigmatism and other

aberrations.

Aberration Δz in z direction from the image point z_1' formed by the central ray is approximately

$$\Delta z = \rho_{10}' \frac{\partial}{\partial l} (\psi_{25} + \psi_{25}') l^2 \tag{44}$$

Only the component $\Delta z'$ which is perpendicular to the isochromat affects the spectral resolution, and this component is from (21) (27) (38) and (40)

$$\Delta z' = |l| H_2 \tag{45}$$

where

$$\begin{aligned} H_2 \equiv & \frac{\rho_{10}' |z_1'|}{f^4} C_0 D_0' \tan\theta \left\{ 1 + \frac{4 z_1'^2}{f^2} C_0^2 D_0^{2\prime} \tan^2\theta \right\}^{-\frac{1}{2}} \left[h_2 (y_1 + y_{10}) \left(1 + \frac{4(f-h_1)}{f} \right) \right. \\ & + \frac{1}{2} (y_1^2 + y_{10}^2) \left(1 - \frac{3(f-h_1)}{f} \right) - \frac{1}{2} z_1^2 (1 + D_0) \left(9 + \frac{39(f-h_1)}{f} \right) \\ & \left. - \frac{z_1^2}{f} C_0 D_0' \tan\theta \left\{ h_2 \left(1 + \frac{4(f-h_1)}{f} \right) + y_{10} \left(1 - \frac{3(f-h_1)}{f} \right) \right\} + \cdots\cdots \right] \end{aligned}$$

$$\begin{aligned} \rho_{10}'^2 \equiv & f^2 \left\{ 1 + \frac{h_2^2 - 2(3y_1^2 + 4z_1^2)}{4f^2} \right\}^2 + 2(3y_1^2 + 4z_1^2) + y_{10} \rho_{101} + y_{10}^2 \rho_{102} + D_0 z_1^2 \rho_{103} \\ & - \frac{z_1^2}{f} C_0 D_0' \tan\theta \, (\rho_{101} + 2 y_{10} \rho_{102}) + \frac{z_1^4}{f^2} C_0^2 D_0'^2 \tan^2\theta + \cdots\cdots \end{aligned}$$

As mentioned in the previous section, $y_{10} = -y_1$ is the condition for minimizing the wavelength error, but this condition is also for minimizing $\Delta z_1'$.

6. Conclusion

In Ebert type monochromators, if the entrance slit has an appropriate form, wavelength for observation can be varied, independently of the slit length, simply by turning the grating whereby the focal plane is not disturbed. But in Littrow type monochromator, the case is different: favourable conditions can only be obtained by making y_1 and z_1 as small as possible and, when a straight entrance slit is used, by setting the exit slit to conform to the condition $y_{10} = -y_1$ for minimizing the astigmatism. As for the effect of astigmatism on the spectral resolution when y_1 and z_1 are small and the condition $y_{10} = -y_1$ is fulfilled, it is smaller in Littrow type than in Ebert type, but the former has a grave defect: the image form not only becomes parabolic but depends on the turning angle of the grating. The difference in form between the exit slit and the image affects seriously the spectral resolution. For example, the

image curvature of $r_0=142$ cm at grating angle of $\theta=10°$ becomes by calculation 69 cm at 20° and 43 cm at 30°. Therefore, there is a considerable variation of image curvature within one order of the grating. The means that are advisable to cope with this defect to heighten the resolution are:

1. To devise the curvature of exit slit to be variable as in the method adopted by Randall,
2. To use such a curvature for exit slit as to match the curvature of image at blaze wavelength minimizing the difference between the two curvatures at off-blaze wavelengths,
3. To make the slit length variable provided the reduction of light energy is tolerated.

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Pueumatic Cell with Rectangular Aperture

Kunio YOSIHARA

Department of Applied Physics, Faculty of Engineering, Nagoya University, Japan

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Abstract

The characteristics of pneumatic cell with rectangular aperture are investigated. Calculations show that such a cell is equivalent to a cell with circular aperture if the diameter of the aperture is properly chosen.

1. Introduction

The aperture that determines the form of heat absorbing film of pneumatic cells is usually circular, but for spectrophotometric purposes it is obviously of advantage to have it rectangular, for the image of slit is nearly rectangular. In this paper, performance and characteristics of cells with rectangular aperture are discussed in comparison with those of usual cells with circular aperture.

2. Response of the Cell to Periodic Incident Radiation

The calculations are essentially the same as given in the previous papers[1)2)].

Let the origin of the co-ordinates be the center of the pneumatic chamber, and the z-axis be the straight line through the center parallel to the incident light. Let the heat absorbing film be on the xy-plane and the lengths of its sides be $2a$ and $2b$. Let the depth of the pneumatic chamber be $2d$. (*cf.* Fig. 1 of the reference 1. We shall use the cartesian co-ordinates in this work.

The response of the cell to the periodic incident radiation $Q(x, y)\exp(-i\omega t)$ can be obtained by solving the follwing equations.

$$\frac{\partial(\Delta Tg)}{\partial t}=k\nabla^2(\Delta Tg) \tag{1}$$

$$\Delta Tg=0 \quad \text{when} \quad x=\pm a \tag{2}$$

1) K. Yosihara: Science of Light, 7, (1958) 67.
2) K. Yosihara: Science of Light, 8, (1959) 8.

$$\varDelta T_g=0 \quad \text{when} \quad y=\pm b \tag{3}$$

$$\varDelta T_g=0 \quad \text{when} \quad z=d \tag{4}$$

$$\varDelta T_g=\varDelta T_f \quad \text{when} \quad z=0 \tag{5}$$

$$C_f\frac{\partial(\varDelta T_f)}{\partial t}=Q(x,\,y)e^{-i\omega t}+2\kappa_g\left(\frac{\partial(\varDelta T_g)}{\partial z}\right)_{z=0}-2\kappa_r\varDelta T_f \tag{6}$$

The notations are the same as used in the previous papers. By the same procedure used there we obtain

$$\varDelta T_g=Ae^{-i\omega t}\sin\frac{n\pi}{2a}(x+a)\sin\frac{m\pi}{2b}(y+b)\sin\{\gamma(d-z)\} \tag{7}$$

where A is a constant and $\gamma=(i\omega/k)-(n\pi/2a)^2-(m\pi/2b)^2$. ($m$ and n are integers) This solution satisfies the boundary conditions (2), (3) and (4).

Combining this expression with the boundary conditions (5) and (6), wd have

$$-i\omega C_fAe^{-i\omega t}\sin\frac{n\pi}{2a}(x+a)\sin\frac{m\pi}{2b}(y+b)\sin(\gamma d)$$

$$=Q(x,\,y)e^{-i\omega t}-2\kappa_gA\gamma e^{-i\omega t}\sin\frac{n\pi}{2a}(x+a)\sin\frac{m\pi}{2b}(y+b)\cos\gamma d$$

$$-2\kappa_\gamma Ae^{-i\omega t}\sin\frac{n\pi}{2a}(x+a)\sin\frac{m\pi}{2b}(y+b)\sin(\gamma d)$$

For simplicity we assume

$$Q(x,\,y)=Q_0\sin\frac{\pi}{2a}(x+a)\sin\frac{\pi}{2b}(y+b)$$

Then we have

$$m=n=1$$

and

$$A=\frac{Q_0}{2\kappa_g\gamma\cos\gamma d+2\kappa_\gamma\sin\gamma d-i\omega C_f\sin\gamma d}$$

Subsituting this expression in (7) we have

$$\varDelta T_g=\frac{Q_0e^{-i\omega t}\sin\frac{\pi}{2a}(x+a)\sin\frac{\pi}{2b}(y+b)\sin\{\gamma(d-z)\}}{(2\kappa_\gamma-i\omega C_f)\sin\gamma d+2\kappa_g\gamma\cos\gamma d}$$

Hence it follows that

$$\overline{\varDelta T_g}=\int_0^d\int_{-b}^b\int_{-a}^a\varDelta T_g\,dx\,dy\,dz/4abd$$

$$=e^{-i\omega t}\frac{4}{\pi^2}Q_0\frac{1-\cos\gamma d}{\gamma d(2\kappa_\gamma-i\omega C_f)\sin\gamma d+2\kappa_g\gamma^2 d\cos\gamma d} \tag{8}$$

where

$$\gamma^2=\frac{i\omega}{k}-\left[\left(\frac{\pi^2}{2a}\right)+\left(\frac{\pi}{2b}\right)^2\right] \tag{9}$$

Apart from the numerical factors, this expression is identical with that for the usual pneumatic cell with circular aperture except that γ^2 is not $-\mu_1^2+(i\omega/k)$ but is given by (9). Now designate ρ for the radius of the pneumatic chamber with circular cross section and define μ_1 so that $\mu_1\,\rho$ becemes the smallest root of $J_0(r)=0$ where J_0 is the Bessel function of the order 0. (the radius of the pneumatic chamber was a in the previous papers.) Then, since $4/\pi^2$ is numerically almost equal to $2J_1(\mu_1\rho)/\mu_1\rho$, the numerical factors are practically the same for both cells. Hence we see that, on a suitable assumption concerning the intensity distaibution of the incident light over the heat absorbing film, the pneumatic cell with rectangular aperture of the area $2\,a\times 2\,b$ is equivalent to the cell with circular aperture of the radius ρ, if ρ is given by the following expression.

$$\left(\frac{\pi}{2a}\right)^2+\left(\frac{\pi}{2b}\right)^2=\left\{\frac{\text{the smallest root of } J_0=0}{\rho}\right\}^2$$

3. Time Constant

The time constant τ of the cell with rectangular aperture can be calculated by the same procedure as used for the cell with circular aperture. (*cf.* reference (1)). The results is

$$d=\frac{1}{\sqrt{(1/k\tau)-(\pi/2a)^2-(\pi/2b)^2}}\,\mathrm{Arccot}\,\frac{(C_f/\tau)-2\kappa_r}{2\kappa_g\sqrt{(1/\kappa\tau)-(\pi/2a)^2-(\pi/2b)^2}}$$

This is identical with the expression (11) of the reference (1) except that μ_1^2 is replaced by $(\pi/2a)^2+(\pi/2b)^2$. Here also, we find that a cell with rectangular aperture is equivalent to a cell with circular aperture of which the radius is given by (10).

4. Numerical Examples

With the help of the expression (10), we can calculate the diameter of the pneumatic chamber of the cell with circular aperture which corresponds to the cell under consideration provided that $2a$ and $2b$ are given.

The following table gives several examples. It is to be noted that ρ is largely determined by the length of the smaller side of the rectangle and is not so much

dependent on the larger one.

Since the relative magnitudes of $2a$, $2b$, and 2ρ——not their absolute values——are singnificant, the dimension of these quantities is omitted.

$2a$	$2b$	2ρ
1	1	1.08
1	2	1.37
1	3	1.45
1	4	1.48
1	5	1.50
1	10	1.52
1	∞	1.53
2	2	2.16
2	3	2.55
2	4	2.74
2	5	2.84
2	10	3.01
2	∞	3.06
3	3	3.25
3	4	3.67
3	5	3.94
3	10	4.40
3	∞	4.60

5. Summary

The results obtained above and those given in the previous papers, shows that, if necessary, we can construct a pneumatic cell with rectangular aperture to suit to the spectroscopic work in hand. Since it is relatively easy to construct a cell with a large heat absorbing film, the calculations above are especially useful in designing a cell to be employed in far infra-red spectroscopy.

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Rotational Structure of the Band Spectrum of S_2 Molecule. Part II.

Katumi IKENOUE

Defense Academy
Kanagawa-ken, Japan

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Abstract

The band spectrum of S_2 molecule is studied in the region from 3700 Å to 4500 Å. The values of the rotational constants of the lower state given in Part I are revised as
$B_e''=0.2956\,\mathrm{cm}^{-1}$ $D_e''=-0.226\cdot10^{-6}\mathrm{cm}^{-1}$ $\alpha_e''=0.164\cdot10^{-2}\mathrm{cm}^{-1}$ $\beta_e''=0.527\cdot10^{-8}\mathrm{cm}^{-1}$
and those of the upper state as

$$B_e'=0.2239\,\mathrm{cm}^{-1} \quad \alpha_e'=0.23\cdot10^{-2}\mathrm{cm}^{-1}$$

The perturbation of the upper state is not homogeneous.

Furthermore, new weak bands of S_2 molecule are studied; it is doubtful whether these bands produce the perturbation on the main band.

1. Rotational analyses of the main band

In continuation to Part I[1], results of further rotational analyses on (0–7) (0–8) (0–9) and (0–10) bands that were not reported in Part I, and results obtained on (1–11) (1–12) (1–13) and (1–14) bands are given in Table VI and Table VII respectively.

Analyses for lower values of K of (1–14) were already reported by Naudé[2] with the results that accord well with the author's.

Further, since the splitting constants, γ' and γ'', obtained are of positive values, it is considered that suffixes 1, 3 such as suffixed to R as R_1 and R_3 in Part I should be revised as given in this Part II.

The rotational levels of $^3\Sigma$ state are given by

$$F_i=B_vK(K+1)+f_i(K,\,J-K)+D_vK^2(K+1)^2+\ldots$$

As was shown by Kramers, $f_i(K,\,J-K)$ for $^3\Sigma$ state is composed of two parts, one of which is due to the interaction of resultant electronic spin S^* with the rotational angular momentum K^* and is equal to

$$\left(\frac{1}{2}\right)\gamma[J(J+1)-K(K+1)-S(S+1)]$$

1) K. Ikenoue: J. Phys. Soc. Japan, 8, 646. (1953)
2) M. Naudé and A. Christy: P. R. 37, 490. (1931)

Table VI.
(0–7) band 3737.3 A

K	ν (cm⁻¹)					
	R_1	R_2	R_3	P_1	P_2	P_3
45	26657.55			26617.98		
43	68.36			30.39		
41	78.54	26650.45		42.17	26615.18	
39	88.05	61.00		53.36	27,31	
37	96.99	70.89		63.99	38.73	
35	26705.37	80.03		74.05	49.52	
33	13.18	88.54		83.59	59.62	
31	20.50	96.42	26708.58	92.64	69.18	26681.53
29	27.29	26703.69	15.90	26701.16	78.11	90.47
27	33.58	10.36	22.54	09.19	86.44	98.77
25	39.33	16.43	28.57	16.68	94.28	26706.47
23	44.59	21.93	34.01	23.67	26701.41	13.57
21	49.35	26.86	38.80	30.18	08.04	20.11
19	53.64	31.25	43.05	36.26	14.15	26.07
17	57.45	35.11	46.70	41.81	19.72	31.47
15	60.81	38.40	49.69	46.92	24.75	36.26
13	63.74	41.19	52.21	51.61	29.29	40.58
11	66.29	43.48	54.11	55.93	33.33	44.34
9	68.58	45.24		59.95	36.87	
7		46.52			39.87	
5		47.24			42.37	

(0–8) band 3834.6 A

K	ν (cm^{-1})					
	R_1	R_2	R_3	P_1	P_2	P_3
103				25408.73		
101	25522.67			35.04		
99	46.80			60.47		
97	70.06			85.07		
95	92.48			25508.99	25520.13	
93	25614.28	25625.38		32.38	44.12	
91	35.47	47.20		55.22	67.42	
89	56.16	68.31		77.65	90.06	
87	76.36	88.75		99.56	25612.09	
85	96.12	25708.64			33.66	
83		27.99			54.78	
81		46.94			75.26	
45	25980.79			25941.19		
43	91.30			53.31		
41	26001.16	25972.96		64.80	35937.72	
39	10.43	83.29		75.73	49.60	
37	19.13	92.92		86.09	60.75	
35	27.29	26001.84		95.99	71.31	
33	34.92	10.13	26022.38	26005.26	81.24	25993.76
31	42.01	17.78	30.17	14.16	90.55	26003.13
29	48.62	24.89	37.29	22.52	99.27	11.85
27	54.73	31.36	43.73	30.34	26007.49	19.98
25	60.33	37.29	49.61	37.70	15.07	27.53
23	65.46	42.65	54.90	44.52	22.15	34.48
21	70.12	47.50	59.62	50.96	28.68	40.89
19	74.30	51.81	63.70	56.94	34.68	46.79
17	78.04	55.51	67.30	62.44	40.14	52.08
15	81.34	58.77	70.29	67.44	45.09	56.80
13	84.17	61.46	72.70	72.06	49.61	61.05
11	86.62	63.70	74.47	76.24	53.51	64.72
9	88.73	65.33			56.94	
7		66.59			59.96	
5		67.30			62.44	
3		67.57			64.45	

(0–9) band 3936.9 A

K	ν (cm^{-1})					
	R_1	R_2	R_3	P_1	P_2	P_3
101	24864.35			24776.72		
99	87.93			24801.62		
97	24910.63			25.64		
95	32.50			49.02		
93	53.72	24964.75		71.81	24883.47	
91	74.32	85.96		94.10	24906.19	
89	94.49	25006.50		24916.00	28.27	
87	25014.25	26.50		37.47	49.83	
85		45.87			70.92	
83		64.77			91.55	
81		83.19				
45	25309.54			25269.98		
43	19.77			81.83		
41	29.42	25301.06		93.09	25265.79	
39	38.44	11.08		25303.75	77.39	
37	46.89	20.44		13.90	88.29	
35	54.79	29.13		23.49	98.62	
33	62.19	37.22		32.60	25308.33	
31	69.02	44.61	25347.98	41.23	17.43	25320.95
29	75.48	51.58	54.92	49.36	25.96	29.55
27	81.41	57.85	61.23	57.04	33.95	37.45
25	86.83	63.58	66.92	64.22	41.40	44.87
23	91.89	68.85	72.01	70.94	48.30	51.58
21	96.34	73.49	76.55	77.19	54.67	57.85
19	25400.37	77.61	80.51	82.96	60.52	63.58
17	03.95	81.25	83.96	88.31	65.86	68.72
15	07.12	84.35	86.83	93.24	70.72	73.36
13	09.89	86.96	89.12	97.76	75.08	77.48
11	12.25	89.12	90.79	25401.89	78.96	81.06
9		90.79	92.05		82.38	
7		91.89			85.25	
5		92.57			87.67	

(0–10) band 4043.5 A

K	ν (cm^{-1})					
	R_1	R_2	R_3	P_1	P_2	P_3
45	24644.25			24604.67		
43	54.19			16.22		
41	63.52	24634.99		27.19	24599.74	
39	72.29	44.77		37.60	24611.06	
37	80.51	53.88		47.50	21.73	
35	88.19	62.34		56.89	31.83	
33	95.36	70.22	24682.00	65.77	41.31	24653.37
31	24702.04	77.43	89.35	74.15	50.20	62.34
29	08.23	84.11	96.06	82.12	58.53	70.64
27	13.97	90.23	24702.12	89.59	66.32	78.38
25	19.23	95.81	07.68	96.58	73.60	85.57
23	24.07	24700.85	12.60	24703.14	80.33	92.18
21	28.40	05.36	16.97	09.24	86.57	98.25
19	32.29	09.39	20.79	14.89	92.30	24703.81
17	35.77	12.91	24.07	20.12	97.52	08.84
15	38.83	15.90	26.81	24.95	24702.25	13.36
13	41.50	18.41	29.04	29.38	06.52	17.43
11	43.79	20.45	30.70	33.42	10.31	20.94
9		22.04			13.64	
7		23.14			16.51	
5		23.78			18.89	
3		23.91			20.79	

Table VII
(1-11) band 4080.1 A

K	ν (cm⁻¹)					
	R_1	R_2	R_3	P_1	P_2	P_3
79	24200.21			24131.07		
77	17.38			49.90		
75	34.04			68.26		
73	50.22			86.16		
71	65.97			24203.66		24184.28
69	81.29		24261.78	20.76		24201.35
67	96.22		76.66	37.49		17.85
65	24310.78		90.99	53.87		33.82
63	24.98		24304.78	69.88	24262.05	49.28
61	38.81	24330.96	18.05	85.54	77.51	64.23
59	52.27	44.17	30.81	24300.83	92.32	78.69
57	65.38	56.80	43.10	15.75	24306.61	92.71
55	78.12	68.92	54.93	30.31	20.45	24306.29
53	90.50	80.56	66.30	44.53	33.86	19.42
51		91.77	77.26		46.87	32.14
49		24402.58	87.76		59.53	44.38
47	91.54	13.04	97.79	51.17	71.88	56.15
45	24402.58	23.21	24407.38	63.78	83.92	
43	13.04	33.06		75.78	95.68	
41	22.82		13.55	87.16		79.34
39	32.01		23.98	97.97		91.24
37	40.61	39.96	33.68	24408.21	24407.02	24402.40
35	48.65	47.36	42.62	17.90	16.17	12.83
33	56.16	54.30	50.83	27.06	24.85	22.61
31	63.10	60.77	58.40	35.68	33.06	31.74
29	69.54	66.78	65.31	43.81	40.82	40.22
27	75.47	72.32	71.57	51.46	48.11	48.11
25	80.92	77.42	77.23	58.61	54.96	55.41
23	85.90	82.06	82.30	65.31	61.36	62.14
21	90.43	86.23	86.77	71.57	67.29	68.28
19	94.51	89.98	90.67	77.42	72.83	73.91
17		93.28	94.06		77.86	79.03
15		96.10	96.88		82.45	83.68
13		98.50	99.25		86.59	87.85
11		24500.42	24501.11		90.28	91.51
9		01.89	02.46		93.52	94.72
7		02.94			96.34	

(1–12) band 4193 A

K	ν (cm^{-1})					
	R_1	R_2	R_3	P_1	P_2	P_3
81				23465.03		
79	23552.99			83.86		
77	69.68			23502.21		
75	85.88			20.10		
73	23601.58			37.51		
71	16.86			54.54		23535.02
69	31.74		23612.06	71.20		51.63
67	46.22		26.52	87.49		67.70
65	60.35		40.40	23603.42		83.24
63	74.10		53.77	19.01	23611.09	98.30
61	87.53	23679.54	66.65	34.25	26.13	23612.82
59	23700.59	92.39	79.01	49.12	40.54	26.88
57	13.30	23704.67	90.93	63.68	54.50	40.54
55	25.71	16.42	23702.33	77.91	67.96	53.77
53	37.73	27.70	13.41	91.77	81.00	66.53
51		38.58	24.02		93.71	78.90
49	26.63	49.10	34.21	84.81	23706.07	90.82
47	38.10	59.28	43.94	97.75	18.11	23702.33
45	48.87	69.14		23710.06	29.87	
43	59.03	78.72	47.97	21.74	41.34	12.37
41	68.49		58.92	32.83		24.75
39	77.39		69.14	43.37		36.35
37	85.77	84.83	78.52	53.38	51.92	47.26
35	93.58	92.02	87.24	62.81	60.83	57.48
33	23800.83	98.76	95.28	71.74	69.28	67.05
31	07.57	23804.99	23802.59	80.17	77.28	75.95
29	13.81	10.80	09.33	88.09	84.83	84.24
27	19.57	16.17	15.40	95.56	91.91	91.91
25	24.88	21.10	20.85	23802.59	98.65	99.01
23	29.73	25.59	25.73	09.13	23804.88	23805.56
21	34.11	29.62	30.05	15.29	10.69	11.57
19	38.09	33.26	33.82	20.96	16.05	17.07
17	41.58	36.35	37.07		20.96	22.07
15		39.11	39.82		25.47	26.61
13		41.41	42.09		29.51	30.70
11		43.29	43.86		33.14	34.28
9		44.71	45.14		36.35	37.40
7		45.71			39.11	
5		46.27			41.41	
3		46.39			43.29	

(1–13) band 4310.1 A

K	ν (cm^{-1})					
	R_1	R_2	R_3	P_1	P_2	P_3
81				22823.93		
79	22911.36			42.23		
77	27.54			60.07		
75	43.25			77.46		
73	58.51			94.44		
71	73.33		22953.81	22911.02		22891.37
69	87.75		67.97	27.20		22907.55
67	23001.77		81.99	43.04		23.18
65	15.45		95.47	58.51		38.30
63	28.79		23008.41	73.70	22965.75	52.89
61	41.82	23033.80	20.86	88.54	80.40	67.02
59	54.49	46.28	32.82	23003.03	94.44	80.70
57	66.83	58.13	44.34	17.20	23007.96	93.96
55	78.81	69.52	55.45	31.02	21.07	23006.82
53	90.51	80.46	66.14	44.53	33.80	19.27
51		90.99	76.41		46.12	31.28
49	78.81	23101.18	86.25	37.01	58.13	42.88
47	90.01	10.98	95.66	49.65	69.84	54.04
45	23100.46	20.55		61.64	81.26	
43	10.29	29.80	99.15	73.07	92.43	63.56
41	19.51		23109.83	83.87		75.64
39	28.17		19.75	94.14		86.99
37	36.28	35.24	28.92	23103.88	23102.28	97.66
35	43.83	42.12	37.41	13.09	10.98	23107.64
33	50.88	48.63	45.20	21.81	19.16	16.97
31	57.42	54.69	52.35	30.02	26.94	25.68
29	63.46	60.26	58.84	37.75	34.30	33.76
27	69.04	65.44	64.72	45.04	41.23	41.23
25	74.17	70.20	69.98	51.90	47.74	48.14
23	78.90	74.52	74.68	58.31	53.83	54.53
21	83.12	78.41	78.90	64.29	59.49	60.45
19	86.94	81.91	82.58	69.82	64.72	65.79
17	90.32	84.95	85.67	74.92	69.55	70.68
15	93.31	87.58	88.31		73.93	75.11
13		89.79	90.49		77.91	79.08
11		91.59	92.18		81.48	82.58
9		92.96	93.31		84.60	85.67
7		93.87			87.26	

(1-14) band 4433.5 A

K	ν (cm^{-1})					
	R_1	R_2	R_3	P_1	P_2	P_3
81				22188.86		
79	22275.81			22206.68		
77	91.50			24.04		
75	22306.72			40.93		
73	21.47			57.41		
71	35.83			73.52		
69	49.81			89.27		22269.48
67	63.41		22343.47	22304.69		84.65
65	76.67		56.48	19.75		99.31
63	89.60		69.01	34.50	22326.40	22313.50
61	22402.22	22394.04	81.05	48.93	40.62	27.22
59	14.50	22406.11	92.66	63.03	54.26	40.52
57	26.44	17.59	22403.78	76.82	67.41	53.38
55	38.09	28.60	14.50	90.30	80.15	65.86
53	49.41	39.20	24.81	22403.45	92.51	77.92
51		49.41	34.72		22404.53	89.60
49	36.99	59.27	44.24	22395.14	16.23	22400.87
47	47.79	68.81	53.36	22407.44	27.62	11.74
45	57.95	78.05		19.12	38.77	
43	67.49	87.03		30.24	49.66	20.51
41	76.43		66.53	40.79		32.33
39	84.83		76.16	50.79		43.41
37	92.67	91.40	85.08	60.28	58.46	58.82
35	22500.01	22498.08	93.32	69.26	66.91	63.56
33	06.85	22504.36	22500.89	77.75	74.89	72.67
31	13.18	10.19	07.83	85.76	82.47	81.16
29	19.04	15.59	14.14	93.32	89.63	89.05
27	24.44	20.58	19.82	22500.44	96.36	96.36
25	29.39	25.13	24.95	07.10	22502.69	22503.12
23	33.95	29.29	29.54	13.36	08.62	09.35
21	38.02	33.07	33.58	19.21	14.14	15.11
19	41.71	36.42	37.11	24.59	19.21	20.36
17	44.96	39.34	40.13	29.54	23.93	25.13
15	47.81	41.86	42.62	34.14	28.20	29.39
13		43.97	44.71		32.08	33.33
11		45.67	46.33		35.53	36.75
9		46.94	47.48		38.56	39.75
7		47.81			41.20	
5		48.29			43.44	

while the other part is due to the interaction between individual spins of the electrons and is designated by $\omega_i(K, J-K)$.

$f_i(K, J-K)$ then becomes

$$f_i(K, J-K)=\frac{1}{2}\gamma[J(J+1)-K(K+1)-S(S+1)]+\omega_i(K, J-K)$$

$$\text{for } J=K+1, \qquad \omega_1=-\varepsilon\left(1-\frac{3}{2K+3}\right)$$

$$\text{for } J=K-1, \qquad \omega_3=-\varepsilon\left(1+\frac{3}{2K-1}\right)$$

$$\text{for } J=K, \qquad \omega_2=2\varepsilon$$

From these reults, the combination differences are given by the equations,

$$\left.\begin{aligned}
\Delta_2F_1(K)&=4B_v\left(K+\frac{1}{2}\right)+8D_v\left(K+\frac{1}{2}\right)^3+2\gamma-\frac{3\varepsilon}{\left(K+\frac{5}{2}\right)\left(K+\frac{1}{2}\right)}\\
\Delta_2F_3(K)&=4B_v\left(K+\frac{1}{2}\right)+8D_v\left(K+\frac{1}{2}\right)^3-2\gamma+\frac{3\varepsilon}{\left(K-\frac{3}{2}\right)\left(K+\frac{1}{2}\right)}\\
\Delta_2F_2(K)&=4B_v\left(K+\frac{1}{2}\right)+8D_v\left(K+\frac{1}{2}\right)^3
\end{aligned}\right\}\quad\cdots\cdots\cdots(1)$$

The combination differences $\Delta_2F_i'(K)=R_i(K)-P_i(K)$ should be the same for the bands (0–7), (0–8), (0–9), (0–10) and for the bands (1–11), (1–12), (1–13), (1–14); and also the values of $\Delta_2F_i''(K)=R_i(K-1)-P_i(K+1)$ should be the same for the bands (0–9), (2–9); (0–10), (2–10) and (1–14), (2–14).

The above were satisfactorily verified within experimental errors in all cases.

The values of $\Delta_2F_1''(K)-\Delta_2F_2''(K)$ and $\Delta_2F_2''(K)-\Delta_2F_3''(K)$ are given in Tables VIII and IX respectively.

The values of splitting constants, γ'' and ε'', of the lower state may be calculated from the equations (1) and also by using the results of Part I.
These values were obtained as

$$\gamma''=0.027\ \mathrm{cm}^{-1} \qquad \varepsilon''=-27.2\ \mathrm{cm}^{-1}$$

Some errors were found in Part I in the calculations of B_v'' and D_v''. Revised correct values for $v''=7$, 8, 9, 10, 14, and 15, together with newly found values for $v''=11$, 12, and 13, are given in Table X. Some of these values almost agree with the values given by Wilson[3] and Naudé.

3) Wilson: unpublished.

Table VIII

K	$\Delta_2F_1''(K)-\Delta_2F_2''(K)$							
	(0–7)	(0–8)	(0–9)	(0–10)	(1–11)	(1–12)	(1–13)	(1–14)
94		0.04						
92		0.01	0.02					
90		0.05	0.08					
88		0.02	0.02					
86		0.01						
62					0.02	0.07	0.07	0.08
60					0.07	0.08	0.07	0.08
58					0.07	0.05	0.11	0.08
56					0.06	0.11	0.05	0.08
54					0.05	0.08	0.10	0.06
52								
50								
48						0.08	0.15	0.07
46					0.08	0.09	0.10	0.08
44	0.09	0.11	0.10	0.08	0.12	0.12	0.11	0.11
42			0.11					
40	0.06	0.06	0.06	0.07				
38	0.05	0.08	0.09	0.09				
36	0.08	0.11	0.05	0.08	0.10	0.10	0.11	0.11
34	0.11	0.11	0.10	0.08	0.13	0.09	0.14	0.14
32	0.09	0.12	0.14	0.15	0.14	0.12	0.08	0.13
30	0.13	0.12	0.10	0.17	0.14	0.12	0.12	0.16
28	0.17	0.12	0.16	0.15	0.16	0.14	0.15	0.17
26	0.15	0.19	0.16	0.15	0.15	0.13	0.16	0.18
24	0.24	0.18	0.22	0.24	0.19	0.20	0.22	0.25
22	0.23	0.25	0.21	0.23	0.25	0.24	0.23	0.21
20	0.25	0.21	0.24	0.23	0.25	0.23	0.23	0.22
18	0.23	0.27	0.26	0.27		0.32	0.27	0.24
16	0.32	0.27	0.32	0.33			0.36	0.34
14	0.38	0.36	0.41	0.39				
12	0.49	0.47	0.45	0.48				
10	0.74	0.67						

Table IX

K	$\Delta_2F_2''(K)-\Delta_2F_3''(K)$							
	(0–7)	(0–8)	(0–9)	(0–10)	(1–11)	(1–12)	(1–13)	(1–14)
62					0.14	0.10	0.08	0.09
60					0.08	0.07	0.07	0.05
58					0.07	0.08	0.05	0.07
56					0.09	0.13	0.07	0.07
54					0.13	0.10	0.07	0.10
52					0.07	0.09	0.05	0.10
50					0.09	0.08	0.09	0.10
48					0.10	0.09	0.07	0.09
46					0.10			
44								
42								
40	0.07	0.09	0.08	0.09				
38	0.08	0.07	0.05	0.10				
36	0.05	0.07	0.05	0.08	0.12	0.12	0.09	0.12
34				0.09	0.13	0.13	0.09	0.12
32		0.13		0.14	0.13	0.17	0.15	0.14
30	0.14	0.18	0.18	0.19	0.15	0.14	0.16	0.14
28	0.18	0.21	0.21	0.22	0.15	0.18	0.18	0.18
26	0.19	0.17	0.16	0.19	0.19	0.25	0.22	0.18
24	0.11	0.21	0.31	0.22	0.21	0.22	0.24	0.18
22	0.22	0.31	0.22	0.24	0.24	0.25	0.21	0.22
20	0.27	0.32	0.28	0.28	0.30	0.32	0.29	0.28
18	0.33	0.32	0.35	0.35	0.30	0.30	0.35	0.36
16	0.46	0.42	0.38	0.41	0.39	0.40	0.40	0.44
14	0.49	0.47	0.48	0.48	0.48	0.46	0.48	0.45
12	0.66	0.67	0.73	0.66	0.57	0.62	0.58	0.59
10			0.84		0.66	0.71	0.75	0.68

Table X

v''	B_v''	$D_v''\cdot 10^6$	v''	B_v''	$D_v''\cdot 10^6$
7	0.2832	−0.198	12	0.2750	−0.161
8	0.2816	−0.185	13	0.2734	−0.158
9	0.2799	−0.165	14	0.2717	−0.150
10	0.2783	−0.166	15	0.2701	−0.150
11	0.2767	−0.160			

From these values the equilibrium constants B_e'' and D_e'' were obtained as

$$B_e'' = 0.2956\,\mathrm{cm}^{-1} \qquad \alpha_e'' = 0.00164\,\mathrm{cm}^{-1}$$

$$D_e'' = -0.226\cdot 10^{-6}\,\mathrm{cm}^{-1} \qquad \beta_e'' = 0.527\cdot 10^{-8}\,\mathrm{cm}^{-1}$$

2. Molecular constant of the upper electronic state

A strong perturbation was observed in the upper state which made the determination of molecular constants of the upper state very difficult.

The mean value of $\dfrac{\Delta_2 F_2'(K)}{K+\dfrac{1}{2}}$ for $v'=0$ can be calculated by using the results of analyses of (0-7) (0-8) (0-9) and (0-10) bands; for $v'=1$ by using those of (1-11) (1-12) (1-13) and (1-14) bands; and for $v'=2$ by using those of (2-9) (2-10) (2-14) and (2-15) bands. These results are given in Table XI.

These results show that, with regard to F_2 -level, there is a strong perturbation

for $v'=0$ band at $K=41$ and in the neighborhood of $K=81$ and $K=91$,

for $v'=1$ band in the neighborhood of $K=37$,

for $v'=2$ band in the neighborhood of $K=11$ and $K=61$;

with regard to the F_1 -level,

for $v'=0$ band in the neighborhood of $K=47$,

for $v'=1$ band in the neighborhood of $K=51$,

for $v'=2$ band in the neighborhood of $K=61$;

and with regard to the F_3 -level,

for $v'=0$ band in the neighborhood of $K=71$,

for $v'=1$ band in the neighborhood of $K=43$,

for $v'=2$ band in the neighborhood of $K=53$.

The molecular constants B_0' and D_0' can be calculated by means of the leastsq-uare method from the value of $\dfrac{\Delta_2 F_2'(K)}{K+\dfrac{1}{2}}$ for large values of K ($K=69\sim75$ $K=85$, 87) which are considered unperturbed.

The values are

$$B_0' = 0.2227\,\mathrm{cm}^{-1} \qquad D_0' = -2.4\cdot 10^{-7}\,\mathrm{cm}^{-1}$$

For $v'=1$, the values of B_1' and D_1' can be calculated by large values of K($K=55$, 57) and small values of K($K=7\sim21$) as

$$B_1' = 0.2205\,\mathrm{cm}^{-1} \qquad D_1' = -3.0\cdot 10^{-7}\,\mathrm{cm}^{-1}$$

Similarly, for $v'=2$, the molecular constants B_2' and D_2' can be calculated by using the value in the neighborhood of $K=31$ as

Table XI

The mean value of $\dfrac{\Delta_2 F_2'(K)}{K+\dfrac{1}{2}}$

K	$v'=0$	$v'=1$	$v'=2$	K	$v'=0$	$v'=1$	$v'=2$
93	0.8692			47	0.8633	0.8666	0.8615
91	0.8719			45	0.8602	0.8634	0.8640
89	0.8742			43	0.8568	0.8592	0.8663
87	0.8762			41	0.8495		0.8681
85	0.8768			39	0.8530		0.8696
83	0.8768			37	0.8575	0.8783	0.8705
81				35	0.8596	0.8781	0.8716
79	0.8781			33	0.8628	0.8796	0.8723
77	0.8791			31	0.8641	0.8801	0.8725
75	0.8802			29	0.8678	0.8801	0.8725
73	0.8807			27	0.8691	0.8809	0.8725
71	0.8811			25	0.8702	0.8805	0.8714
69	0.8813			23	0.8733	0.8805	0.8699
67	0.8812			21	0.8750	0.8805	0.8656
65	0.8805			19	0.8771	0.8815	
63	0.8794			17	0.8791	0.8803	
61	0.8783	0.8686		15	0.8808	0.8806	
59	0.8769	0.8714	0.8398	13	0.8800	0.8811	
57	0.8750	0.8727	0.8457	11	0.8835	0.8813	
55	0.8729	0.8731	0.8493	9	0.8834	0.8808	
53	0.8710	0.8727	0.8526	7	0.8850	0.8807	
51	0.8686	0.8715	0.8558	5	0.8873	0.8818	
49	0.8662	0.8695	0.8587	3	0.8914		

$$B_2'=0.2181\ \mathrm{cm}^{-1} \qquad D_2'=-2.0\cdot10^{-7}\ \mathrm{cm}^{-1}$$

The values of B_v' are considered to be close to the right values.

From these values the equilibrium constants B_e' and D_e' are obtained as

$$B_e'=0.2239\ \mathrm{cm}^{-1} \qquad \alpha_e'=0.23\cdot10^{-2}\ \mathrm{cm}^{-1}$$

$$D_e'=-0.28\cdot10^{-6}\ \mathrm{cm}^{-1} \qquad \beta_e'=-2.0\cdot10^{-8}\ \mathrm{cm}^{-1}$$

3. Rotational Perturbation

For finding the degree of perturbation of the main band, it is necessary to calculate the values of $R_i(K)$ by $R_i(K)=\nu_0+F_i'\ (K+1)-F_i''(K)$ and to find the differences between the calculated values and the observed values.

These differences are given in Table XII.

Table XII. $R_2(K)$ cal. − $R_1(K)$ obs.

K	$v'=0$	$v'=1$	K	$v'=0$	$v'=1$	K	$v'=0$	$v'=1$
93	−36.98		61	−24.08	−15.96	29	3.59	0.05
91	−37.50		59	−24.38	−16.17	27	2.93	0.06
89	−37.80		57	−24.78	−16.28	25	2.35	0.06
87	−37.93		55	−25.31	−16.33	23	1.89	0.07
85	−38.00		53	−25.96	−16.36	21	1.45	0.09
83	−38.02		51	−26.73	−16.45	19	1.08	0.06
81	−38.14		49	−27.63	−16.64	17	0.79	0.14
79			47	−28.61	−16.95	15	0.59	0.10
77	−23.62		45	−29.73	−17.39	13	0.37	0.10
75	−23.66		43	−30.94	−18.01	11	0.26	0.07
73	−23.66		41	10.40		9	0.14	0.06
71	−23.67		39	8.81		7	0.07	0.04
69	−23.67		37	7.43	0.06	5	0.00	0.02
67	−23.69		35	6.28	0.03	3		0.00
65	−23.74		33	5.22	0.00			
63	−23.86		31	4.35	0.04			

The value of ν_0 differs before and after the perturbation, and the shift does not resume its zero position. This shows that the perturbation is not homogeneous, that is $\Delta\Lambda=\pm 1$, and suggests the existence of another state very near the upper state of the main band, for a strong perturbation occurs only if the vibrational eigenfunctions favorably overlap one over the other.

4. Rotational analyses of (v'–7) (v'–8) and (v'–9) bands

This system of bands is very weak and many lines of the main band are overlapping. Six branches were found starting from the neighborhood of the band-head; their rotational analyses were completed.

Photographs of the bands that were used for analyses were taken in the fifth order of a 21-ft. concave grating.

The results obtained from the analyses of (v'–7) (v'–8) and (v'–9) bands are given in Table XIII.

The values of $\Delta_2 F_i'(K)$ and $\Delta_2 F_i''(K)$ are given respectively in Table XIV and Table XV.

According to the results of these analyses, the lower state of this system of bands is that of the main band which is the ground state ${}^3\Sigma_g^-$.

Table XIII

(v'–7) band λ 3732.7 A

K	ν (cm^{-1})					
	R_1	R_2	R_3	P_1	P_2	P_3
35						
33	26718.68			26689.97		
31	26.86			99.84		
29	34.54	26737.11		26709.19	26711.61	26716.57
27	41.59	43.84	26748.63	18.04	20.25	25.54
25	48.20	50.28	55.43	26.40	28.47	34.01
23	54.32	56.22	61.59	34.29	36.08	42.05
21	59.95	61.59	67.36	41.59	43.20	26749.49
19	65.07	66.29	72.41	48.38	49.69	56.22
17	69.62	70.62	76.93	54.65	55.72	62.49
15	73.67	74.39	80.84	60.31	61.24	68.22
13	77.11	77.69	84.11	65.46	66.29	73.13
11	80.12	80.48	86.76	70.09	70.80	77.54
9	82.60	82.78	88.74	74.17	74.78	81.24
7	84.46	84.46	89.99	77.69	78.15	84.11
5	85.97	85.51	90.49	80.84	80.84	86.22
3	86.76	85.97		83.07	82.92	

(v'–8) band λ 3830.0 A

K	ν (cm^{-1})					
	R_1	R_2	R_3	P_1	P_2	P_3
35				25997.21		
33	26036.21			26007.35		
31	44.11			17.20		
29	51.64			26.31		26030.44
27	58.64		26062.30	35.23		39.19
25	65.19		68.86	43.46	26044.52	47.50
23	71.24	26072.06	74.88	51.13	51.81	26055.14
21	76.68	77.16	80.29	58.40	58.77	62.30
19	81.72	81.92	85.08	65.06	65.46	68.86
17	86.24	86.24	89.41	71.24	71.38	74.88
15	90.16	89.95	93.08	76.95	76.82	80.29
13	93.70	93.08	96.18	82.06	81.72	85.08
11	96.56	95.78	98.60	86.62	86.07	89.41
9	99.04	97.96	26100.68	90.77	89.95	93.08
7	26100.99	99.62	01.87	94.28	93.32	95.95
5	02.42	26100.68	02.42	97.34	95.95	98.16
3	03.34	01.12		99.83	97.96	

$(v'\text{-}9)$ band λ 3931.4 A

K	ν (cm^{-1})					
	R_1	R_2	R_3	P_1	P_2	P_3
35				25325.32		
33	25364.09			35.33		
31	71.88	25374.42		44.87	25347.08	
29	79.22	81.25		53.93	55.73	
27	86.05	87.60		62.61	63.90	25366.66
25	92.44	93.59	25396.05	70.72	71.69	74.68
23	98.34	99.08	25401.89	78.32	78.96	82.38
21	25403.70	25404.12	07.28	85.43	85.73	89.41
19	08.51	08.67	12.06	91.89	91.89	95.86
17	12.80	12.58	16.32	97.76	97.76	25401.89
15	16.58	16.19	19.97	25403.21	03.08	07.28
13	19.85	19.33	22.95	08.18	07.93	12.06
11	22.66	21.95	25.57	12.58	12.25	16.32
9	24.92	24.05	27.44	16.45	16.06	19.85
7	26.66	25.57	28.61	19.85	19.17	22.66
5	27.86	26.47	29.19	22.66	21.82	24.92
3	28.48			24.92		

Table XIV

K	$\Delta_2F_1'(K)$			$\Delta_2F_2'(K)$			$\Delta_2F_3'(K)$		
	$(v'\text{-}7)$	$(v'\text{-}8)$	$(v'\text{-}9)$	$(v'\text{-}7)$	$(v'\text{-}8)$	$(v'\text{-}9)$	$(v'\text{-}7)$	$(v'\text{-}8)$	$(v'\text{-}9)$
33	28.71	.86	.76						
31	27.02	.91	.01			27.34			
29	25.35	.33	.29	25.50		.52			
27	23.55	.41	.44	23.59		.70	23.09	.11	
25	21.80	.73	.72	21.81		.90	21.42	.36	.37
23	20.03	.11	.02	20.14	.25	.12	19.54	.74	.51
21	18.36	.28	.27	18.39	.39	.39	17.87	.99	.87
19	16.69	.66	.62	16.60	.46	.78	16.19	.22	.20
17	14.97	.00	.04	14.90	.86	.82	14.44	.53	.43
15	13.36	.21	.37	13.15	.13	.11	12.62	.79	.69
13	11.65	.64	.67	11.40	.40	.40	10.98	.10	.89
11	10.03	.94	.08	9.68	.71	.70	9.22	.19	.25
9	8.43	.27	.47	8.00	.01	.99	7.50	.60	.59
7	6.77	.71	.81	6.31	.30	.40	5.88	.92	.95
5	5.13	.08	.20	4.67	.73	.65	4.27	.26	.27
3	3.69	.51	.56	3.05	.16				

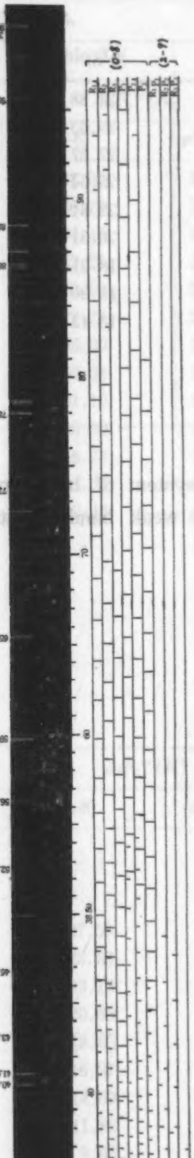
Table XV

K	$\Delta_2 F_1''(K)$					
	(0–7)	(v'–7)	(0–8)	(v'–8)	(0–9)	(v'–9)
34			38.93	39.05	38.70	38.77
32	36.91	36.89	36.75	36.76	36.42	36.55
30	34.64	34.70	34.46	34.44	34.25	34.35
28	32.42	32.40	32.21	32.33	32.05	32.12
26	30.14	30.16	29.99	29.96	29.79	29.83
24	27.89	27.92	27.76	27.78	27.67	27.62
22	25.68	25.66	25.60	25.55	25.40	25.38
20	23.46	23.48	23.34	23.32	23.18	23.08
18	21.19	21.24	21.10	21.18	20.99	20.91
16	19.00	19.02	18.90	18.92	18.81	18.82
14	16.82	16.80	16.73	16.75	16.65	16.64
12	14.68	14.66	14.56	14.50	14.49	14.48
10	12.65	12.51	12.49	12.42		12.34
8		10.29		10.22		10.21
6		8.28		8.14		8.01
4		5.92		6.00		5.82

K	$\Delta_2 F_2''(K)$					
	(0–7)	(v'–7)	(0–8)	(v'–8)	(0–9)	(v'–9)
30					34.15	34.17
28	32.25	32.23			31.89	31.87
26	29.99	30.03			29.63	29.69
24	27.65	27.75	27.58	27.54	27.45	27.39
22	25.45	25.51	25.35	25.35	25.19	25.16
20	23.21	23.09	23.13	23.15	22.94	22.94
18	20.96	20.93	20.83	20.78	20.73	20.69
16	18.68	18.67	18.63	18.57	18.49	18.43
14	16.48	16.45	16.37	16.30	16.24	16.25
12	14.19	14.19	14.09	14.06	14.04	14.02
10	11.91	11.98	11.82	11.89	11.83	11.80
8	9.65	9.68	9.65	9.67	9.51	9.51
6	7.37	7.36	7.34	7.36	7.32	7.30
4		5.13	5.13	5.17		

K	$\Delta_2F_3''(K)$					
	(0–7)	(v'–7)	(0–8)	(v'–8)	(0–9)	(v'–9)
28	32.07	32.06	31.88	31.86		
26	29.80	29.89	29.63	29.67	29.47	29.39
24	27.54	27.58	27.37	27.38	27.14	27.21
22	25.23	25.31	25.04	25.15	24.97	24.90
20	22.94	22.92	22.81	22.78	22.66	22.65
18	20.63	20.71	20.51	20.55	20.38	20.46
16	18.22	18.35	18.21	18.20	18.11	18.08
14	15.95	15.89	15.90	15.89	15.76	15.67
12	13.53	13.63	13.42	13.52	13.31	13.51
10		11.20		11.27	10.99	11.12
8		8.75		8.79		8.76
6		6.38		6.47		6.53

But the upper state of this system of bands remains untraced; it is doubtful, whether the upper state of these weak bands produce the perturbation on the main band.



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